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Short communication

Bipolar porous polymeric frameworks for low-cost, high-power, long-life all-organic energy storage devices

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HIGHLIGHTS

- Porous polymeric frameworks for affordable all-organic energy storage devices.
- All-organic energy storage devices having high-power density and long cycle life.
- A potential organic electrode towards high-performance organic energy storage device.

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ABSTRACT

Organic-based energy storage devices are of great interests due to their high potential as affordable, high-performance energy storage devices. Especially, all-organic energy storage devices, where cathode and anode are constituted of organic compounds, could be an extremely affordable device expected to be applied to smart grids. Recent reports on bipolar porous polymeric frameworks (BPPFs) suggest very promising features of this new organic electrode group towards high-performance energy storage devices. Here, we studied an all-organic system using BPPFs for both anode and cathode parts. The formation of BPPFs was confirmed by Raman spectroscopy and N_2 isotherm measurements. The electrochemical properties of this all-organic energy storage device using BPPFs showed a high-power density of 1 kW kg^{-1} based on the total mass of the BPPFs and a long cycle life of over 1000 times.

1. Introduction

Electrical energy storage is a key technology for the successful introduction of renewable energy concept into our society [1–3]. Energy storage devices for stationary applications need to become extremely affordable and to have a long charge–discharge cycle life features that are more essential than having a higher energy density and a higher power density like in case of batteries for the use in vehicle [4]. It is an urgent need to develop energy storage devices which can be integrated into a grid combined with wind and solar power sources, and that can manage energy storage systems. From this point of view, the discovery of organic materials exhibiting promising electrochemical properties are essential for the development of low-cost, and long-life batteries because of their abundance [5–8]. Moreover, lithium-free all-organic electrodes, which are constituted of only abundant materials, would be a leading candidate for an extremely affordable battery. Here, we show an all-organic battery provided by bipolar porous polymeric frameworks (BPPFs) using covalent triazine-based frameworks (CTFs) [9].

Recently, we have found BPPFs, i.e., porous polymeric frameworks constituted of benzene, as electron donor, and triazine rings, as electron acceptor, as a bipolar semiconducting organic material and have proposed a new energy storage principle using BPPFs [10,11]. Redox active organic materials are often categorized in carbonyl, radical, or organosulfur compounds [6]. However, BPPFs are aromatic compounds comparable to porous graphene [11]. Additional studies on redox-active aromatic compounds [12–14] could pave the way for the further development of organic

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energy storage devices. From the perspective of the industry side, BPPFs have potential for affordable and high-performance batteries, since it shows both high specific power and energy [10,11]. Suga et al. demonstrated a simple, symmetric all-organic battery with an intercalation mechanism by using a new bipolar radical polymer [15], and most recently all-organic batteries using bipolar polyparaphenylene were reported [16]. The features of BPPFs are a promising strategy for the further improvement of all-organic batteries. BPPFs have the following advantages for use as electrode material and in cell fabrication: (I) a high specific power due to rapid ion transport promoted by its porous nature, (II) a long battery life due to the high stability of the framework, (III) a simple, safe and low-cost configuration by using the same organic materials for the cathode and the anode. Hence, the BPPFs for both cathode and anode provide a safe, high-performance and long-life all-organic battery.

Here, we show results for developing all-organic Li- and Na-batteries using BPPFs. The all-organic Li-batteries can provide a specific energy of 34 Wh kg^{-1} and a specific power of 1 kW kg^{-1} based on the total mass of the BPPF with a cycle-life of over 1000 times. The all-organic Na-batteries also showed electrochemical properties which are comparable to the all-organic Li-batteries.

2. Experimental

The BPPFs were synthesized by heating a mixture of *p*-dicyanobenzene and zinc chloride in quartz ampules at 400 °C for 40 h [9]. The obtained samples were washed with 1 M HCl and distilled water for several times. After drying, we used this material as BPPFs without further treatments.

The following measurements were performed to characterize BPPFs. Raman spectroscopy measurements were carried out by using a Ventuno (NSR-1000DT, JASCO) with a laser excitation of 632.8 nm from a He–Ne laser. Powder X-ray diffraction (XRD) measurements were done on a PANalytical X'Part PRO diffractometer using Cu $K\alpha_1$ radiation. Nitrogen physisorption measurements were conducted at 77 K up to 1 bar using a Quantachrome Autosorb 1C apparatus.

Electrodes were made by mixing the active material (70 wt.%), carbon (carbon black; 20 wt.%), and a binder (carboxyl methyl cellulose; 10 wt.%) using Al current collectors. We assembled the cells in a purge-type dry glove box filled with high purity Ar gas and tested them on a multichannel potentiostatic–galvanostatic system (SD-8, Hokuto-denko). 1 M $NaClO_4$ in propylene carbonate (PC) or 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio 1:1 (Kishida Chemicals) were used as electrolytes in a two-electrode-type Swagelok cell as test cell. The specific energy E (Wh kg^{-1}) can be calculated by $E = \int_0^{t_{cut}} (I_0/m)V(t)dt$ where t_{cut} (h) is the discharge time, I_0 (A) is the constant current, m (kg) is a mass of the active material at a single electrode, and $V(t)$ is a time-dependent voltage in the dimension of V. Specific power P (W kg^{-1}) can be calculated by $P = E/t_{cut}$. We show a Ragone plot with the total mass of BPPFs in a cell. To measure the electrochemical properties, the cells were charged up to 1.75 V and discharged until −1.75 V. Thus, the cells show a cell voltage ranging between 0 and 3.5 V.

3. Results and discussion

The BPPFs have been synthesized following already reported procedures [9–11] and characterized by nitrogen physisorption and Raman spectroscopy, and X-ray diffraction (XRD). The Raman spectroscopy measurement reveals the formation of a short-range ordered two-dimensional (2D) graphitic network in the BPPF by showing relatively strong *D* and *G* peaks at around 1300 cm^{-1} and 1600 cm^{-1}, respectively (Fig. 1a) [11]. The nitrogen physisorption measurements show a high specific surface area of over 1000 $m^2\ g^{-1}$ and a typical isotherm shape suggesting a microporous structure. The physisorption measurements confirm the successful formation of a porous network (Fig. 1b). The broad XRD pattern suggests that the BPPF is comprised of non-coplanar two-dimensional (2D) organic frameworks made up of aromatic rings like hard carbon (Fig. 1c) [17]. These results agree well with previous studies on the characterization of porous polymeric frameworks [9–11].

The fundamental electrochemical characteristics of the all-organic Li-batteries using BPPF are studied by investigating the charge–discharge properties. Charge–discharge profiles at various current densities from 0.05 A g^{-1} to 2 A g^{-1} in the working voltage range of 0.0–3.5 V are shown in Fig. 2a. At a constant current density of 0.05 A g^{-1}, the all-polymer system shows a specific capacity of ~65 mA h g^{-1} based on the mass of the BPPF at a single electrode with a sloping voltage profile. If we calculate the amount of the coordinated Li^+ into the BPPF (=x in Eqs. (1)–(3)), we obtain $x \sim 1.86$ mol. The unit is defined by trimerized *p*-dicyanobenzene, which has a molecular weight of 384.09 g mol^{-1}. This result also suggests that our battery system uses 1.86 mol of the electrolyte for 1 mol of the BPPF at the current density of 0.05 A g^{-1} (Eq. (3)).

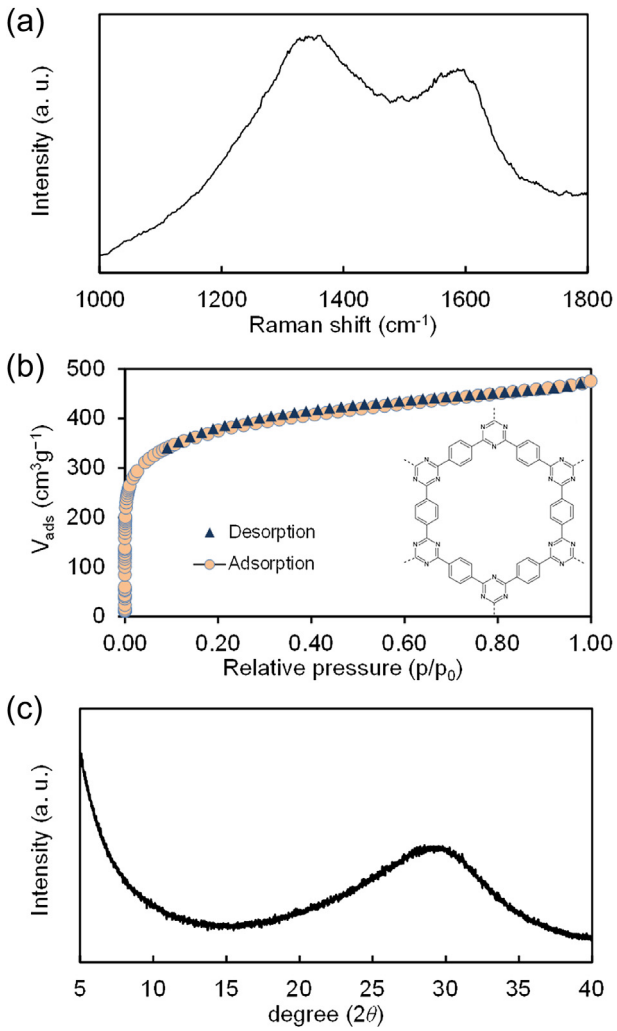

Fig. 1. Characterization of the BPPF. (a) Raman spectrum, (b) N_2 physisorption isotherm with a schematic illustration of the BPPF, and (c) XRD pattern.

Under a high rate condition of 2.0 A g^{-1}, our system shows a specific capacity of ~17 mA h g^{-1}.

The stability of the battery at high rates and a long charge–discharge cycle is shown in Fig. 2b and c, respectively. Even for cycling under high rate condition, the BPPF-based all-organic battery shows stable cycling again (Fig. 2b). Moreover, this battery system shows an excellent cycle performance up to 1000 cycles at the current density of 1.0 A g^{-1} (Fig. 2c). These two results reveal the remarkable property of BPPF-based battery with respect to both rate performance and long cycle life. The comparison of the specific power and the specific energy (Ragone plot) of the BPPF-based all-polymer battery are shown in Fig. 3. For instance, other organic battery systems, such as Poly(3-methylthiophene)-based polymer supercapacitors exhibit a specific energy of 13 Wh kg^{-1}, and a specific power of 1.4 kW kg^{-1} based on the total mass of the polymer [18]. The poly(nitronylnitroxylstyrene)-based bipolar polymer battery [15], which works with an intercalation mechanism, exhibits a specific energy of 57.2 Wh kg^{-1} based on the total mass of the polymer [19]. Our energy storage device shows comparable electrochemical properties to these all-polymer energy storage devices using already sophisticated redox-active polymers. Our all-polymer battery will provide a specific energy of 34 Wh kg^{-1} and a specific power of 1 kW kg^{-1} based on the total mass of the BPPF, thus providing both high specific power and energy as all-organic energy storage device (Fig. 3a).

Based on our former studies [10,11], we propose an electrical energy storage reaction for the BPPF. The reaction of the electrodes is expected to be based on the oxidized (*p*-doped) state of the benzene rings (electron donor) in BPPF:

$$\left[\mathrm{BPPF}^{+x}\left(\mathrm{PF}_6^-\right)_x\right] + xe^- \leftrightarrow (\mathrm{BPPF}) + x\mathrm{PF}_6^- \quad (1)$$

and to be based on the reduced (*n*-doped) state of the triazine rings (electron acceptor):

$$(\mathrm{BPPF}) + xe^- + x\mathrm{Li}^+ \leftrightarrow \left[\mathrm{BPPF}^{-x}\left(\mathrm{Li}^+\right)_x\right] \quad (2)$$

From Eqs. (1) and (2), the net reaction is:

$$\left[\mathrm{BPPF}^{+x}\left(\mathrm{PF}_6^-\right)_x\right] + \left[\mathrm{BPPF}^{-x}\left(\mathrm{Li}^+\right)_x\right] \leftrightarrow 2(\mathrm{BPPF}) + x\mathrm{Li}^+\left(\mathrm{PF}_6^-\right) \quad (3)$$

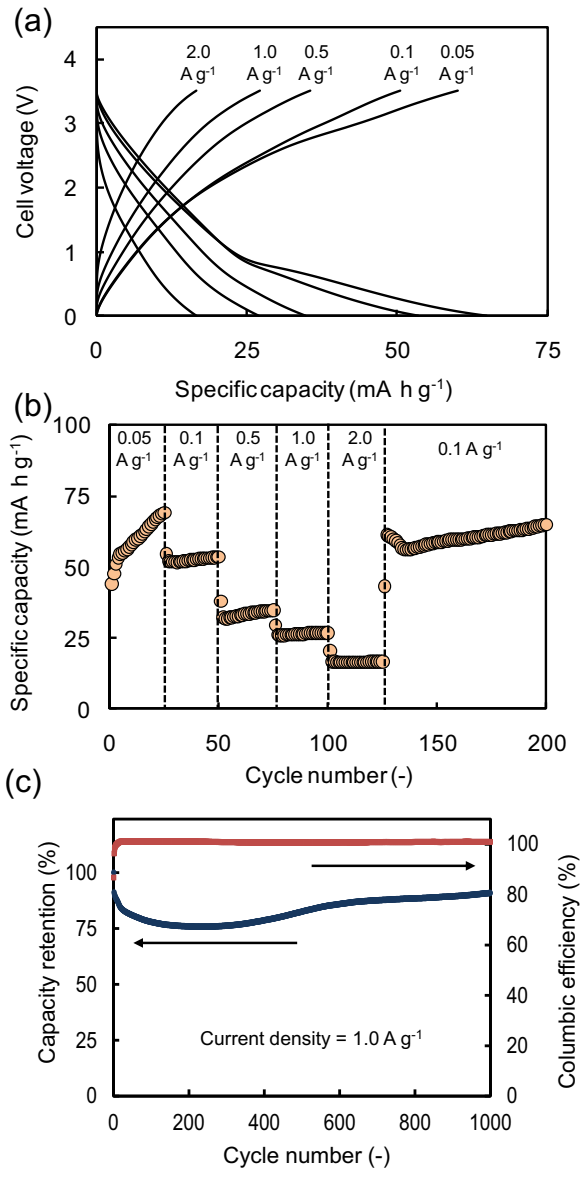

Fig. 2. Electrochemical characterization of all-organic Li-batteries. (a) Charge–discharge profiles of all-organic Li-batteries, (b) cycle performance of all-organic Li-batteries, and (c) cycle life and coulombic efficiency of all-organic Li-batteries. The electrochemical properties are shown based on the mass of BPPFs at a single electrode.

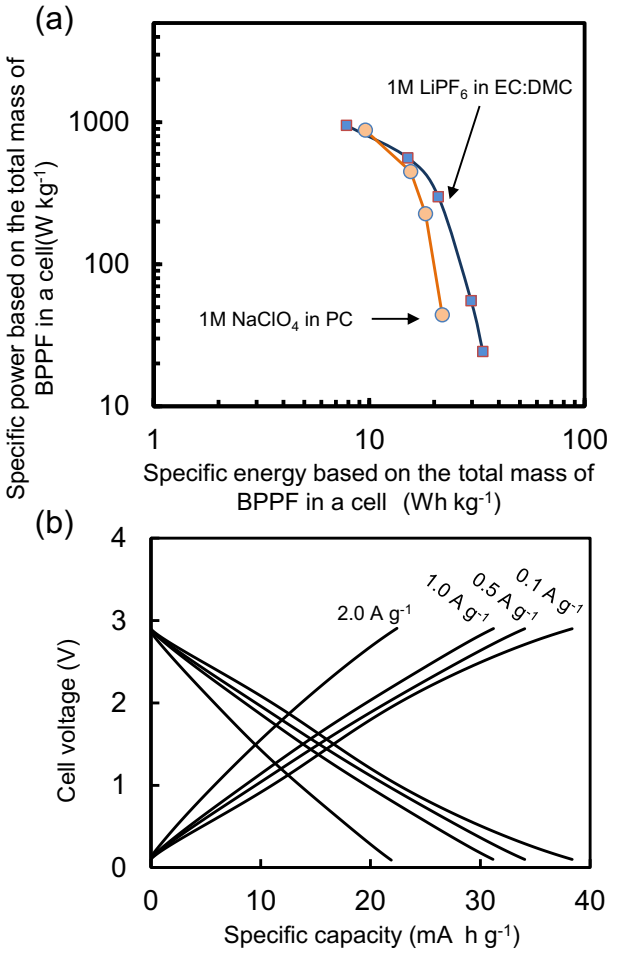

Fig. 3. (a) Ragone plots for all-organic Li- and Na-batteries and (b) charge–discharge profiles of all-organic Na-batteries. The properties in the Ragone plot are shown based on the total mass of BPPFs in a cell.

To describe the electrochemical reaction for the all-organic energy storage device, a cell arrangement of organic electrodes A and B is considered. First of all, we charged the cell up to 1.75 V, then the organic electrode A undergoes reaction Eq. (1), i.e. the *p*-doping reaction, and the other organic electrode B follows reaction Eq. (2), which is the *n*-doping reaction. During the discharge reaction, from 1.75 to 0 V, the electrochemical reaction at the electrode A is based on Eq. (1); however from 0 to −1.75 V, the electrochemical reaction at the electrode A becomes Eq. (2), which is the *n*-doping reaction. Thus, the cells show a cell voltage ranging from 0 to 3.5 V as described in Fig. 2a. By applying this energy storage mechanism, a stable cycle performance can be achieved due to a low doping state which gives less stress on the organic electrodes compared to a deep doping state in general.

Beside lithium, also sodium can be applied to all-organic battery using BPPFs as charge carrier. Few researches have reported organic materials used in next-generation batteries, such as lithium-air batteries [20]. To the best of our knowledge, this is the first report about all-organic batteries using sodium as charge carriers. We have used 1 M $Na(ClO_4)$ in PC as an electrolyte for the all-organic Na-batteries in a cell voltage region of 3 V. The electrochemical properties of all-organic batteries using sodium are as good as the properties using lithium (Fig. 3b). Our sodium-based all-polymer batteries provide a specific energy of 22 Wh kg^{-1} and a specific power of 0.9 kW kg^{-1} based on the total mass of the BPPF (Fig. 3a, b). Recently, sodium-based batteries are of great interest due to their highly affordability compared to lithium-based batteries. From this point of view, our result indicates that all-organic batteries using sodium as a charge carrier can be a candidate for an extremely affordable energy storage device.

4. Conclusion

In conclusion, the BPPF-based all-organic batteries presented in this work demonstrate high-performance electrochemical properties with a simple full-cell configuration: the use of same organic compounds in both anode and cathode. This performance was achieved by a combination of the porous structure and the unique electronic properties of the BPPFs. Moreover, we found that the concept of BPPFs can be applied to sodium-based all-organic energy storage devices. Hence, we believe that our study on BPPFs will initiate a new strategy towards extremely affordable, safe, high-performance all-organic energy storage device.

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